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Oxygen Vacancy-Driven Evolution of Structural and Electrical Properties in SrFeO_{3-δ} Thin Films and a Method of Stabilization

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Epitaxial SrFeO_{3-δ} (SFO) thin films have been grown on various substrates by pulsed laser deposition. Structural and electrical properties of SFO thin films are monitored with time in different atmospheres at room temperature, showing time-dependent crystal structure and electrical conductivity. The increased out-of-plane lattice parameter and resistivity over time are associated with the increased oxygen vacancies density in SFO thin films. The epitaxial strain plays an important role in determining the initial resistivity and sample environment determines the trend of resistivity change over time. An amorphous Al₂O₃ passivation layer has been found to be effective in stabilizing the structure and electrical properties of SFO thin films. This work explores time dependent structure and properties variation in oxide films and provides a way to stabilize thin film materials which are sensitive to oxygen vacancies.

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$\text{SrFeO}_{3-\delta}$ (SFO) perovskite thin films have a wide range of desirable physical properties that have garnered great interest from the scientific community. The existence of multiple valence states of Fe, which allows for various stable states of oxygen occupancy in the lattice, makes SFO a highly sought-after catalytic and gas-sensing material.¹⁻⁵ The contribution from the Fe in the SFO crystal also results in useful magnetic properties.⁶⁻⁸ It is important to note that much of the recent attention in $\text{SrFeO}_{3-\delta}$ thin films stems from its strong dependence of the crystal structure, magnetic and electrical properties on the oxygen content ($0 \leq \delta \leq 0.5$). $\text{SrFeO}_{2.5}$ exhibits semiconducting behavior and brownmillerite structure, while SrFeO_3 shows metallic behavior with simultaneous existence of helical antiferromagnetic-ordered spin structure.⁹⁻¹² The unique magnetic structure has made the metallic SrFeO_3 an attractive material for spintronic and other technological applications, but challenges in the synthesis and stability of this state have impeded research efforts in thin films. Pulsed laser deposition (PLD) is a powerful thin film synthesis technique with the potential to grow highly epitaxial SrFeO_3 structures, but PLD synthesis under normal conditions usually leads to oxygen deficient SFO thin film, which has prompted supplementary efforts to saturate oxygen via strong oxidizing environments such as ozone annealing.¹³

Here, we systematically investigate the oxygen-dependent evolution of structural stability and electronic properties in epitaxial SFO thin films. We investigate the contribution of epitaxial strain on the changes in crystal structure and physical properties over time at room temperature in O_2 and air. An amorphous Al_2O_3 passivation layer is found to be effective in preventing the degradation of SFO thin films.

SFO thin films were grown by PLD using a KrF excimer laser (Lambda Physik LPX 300, $\lambda = 248$ nm, 2 Hz). The SFO target used for the deposition was fabricated by a conventional ceramic sintering process. The laser beam was image-focused onto the target to get a uniform energy density of 2.0 J/cm^2 .¹⁴⁻¹⁶ Prior to the deposition, the chamber was pumped down to a base pressure of 1×10^{-6} Torr. A substrate temperature of 800°C and an oxygen pressure of 250 mTorr were maintained during all depositions. Both the target and the substrate were rotated during the deposition to achieve better uniformity. The average growth rate is approximately 0.21 \AA per laser pulse. After deposition, an oxygen pressure of 250 Torr was introduced

and the films were held at 600 °C for 1 hour to allow full oxygenation of the thin film. The films were then cooled down to room temperature at 5 °C/min. In order to study strain effects on the physical properties of the SFO films, different substrates such as $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}$ (LSAT), LaAlO_3 (LAO), SrTiO_3 (STO), and MgO were used. An amorphous Al_2O_3 passivation layer was also deposited on SFO/LSAT. The Al_2O_3 passivation layer with an approximate thickness of 300 nm was deposited at 400 °C and an oxygen pressure of 250 mTorr with the same laser energy density of 2.0 J/cm².

X-Ray diffraction (Panalytical X'Pert PRO MRD) including 2θ - ω and reciprocal space mapping (RSM) was employed to study the orientation, lattice parameters and epitaxial quality of the thin films. High-resolution transmission electron microscopy (HRTEM) (FEI Tecnai G2 F²⁰, 300 kV) was used to investigate the film microstructure. Selected area electron diffraction (SAED) patterns were recorded to identify epitaxial relationship. Time dependent resistance measurements were carried out (Keithley 2420 current source meter) in O₂ and air environments at room temperature.

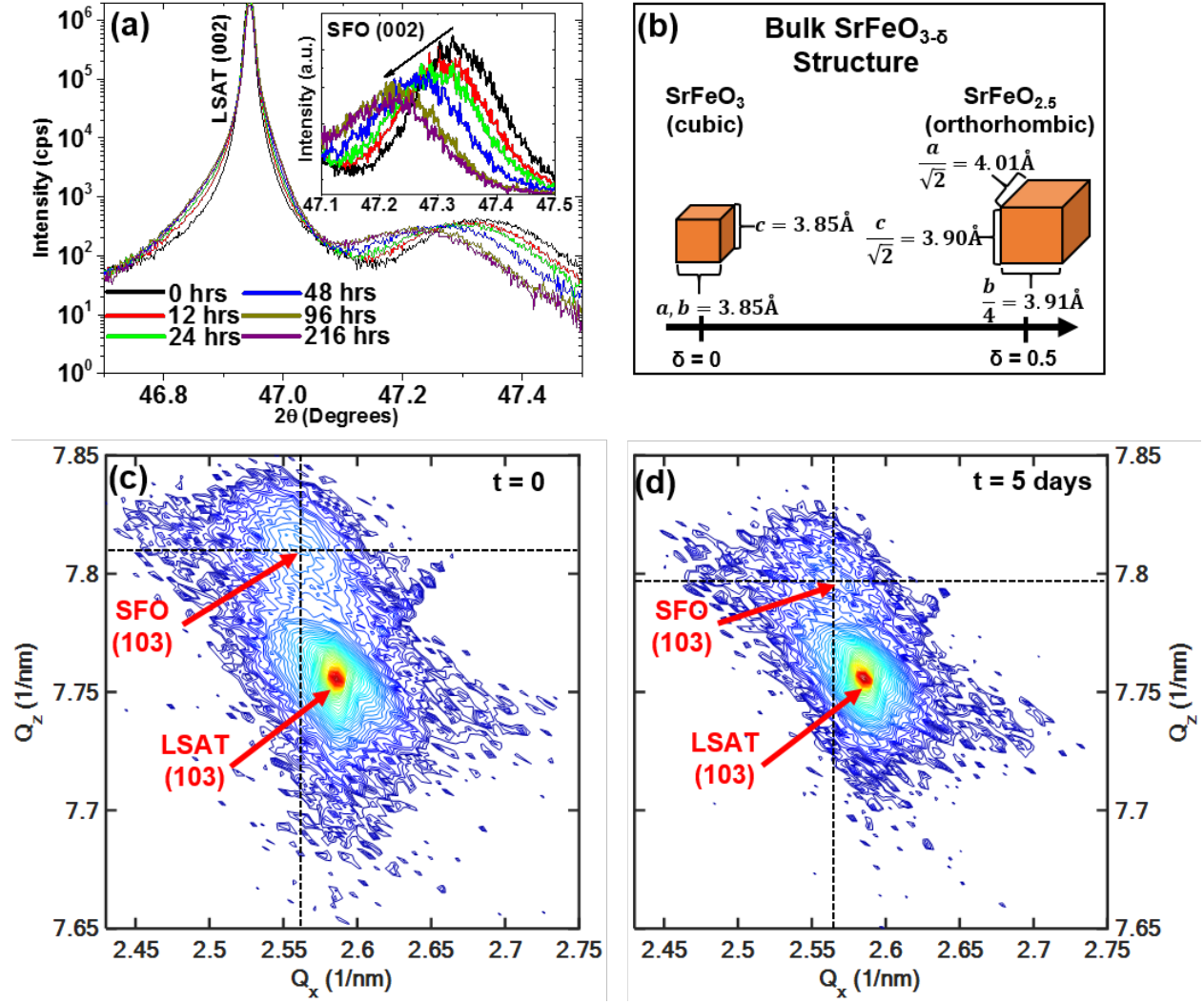


Figure 1. a) 2 θ - ω XRD scan of SFO film grown on LSAT (001) substrate with peak shifting over time after initial synthesis. b) Illustration of increasing unit cell parameters reported in bulk SrFeO_{3- δ} at $\delta = 0$ and 0.5. c) RSM scan of SFO film on LSAT (001) at $t = 0$ and d) $t = 5$ days after synthesis.

SFO thin films were initially grown on LSAT substrates, which results in a lattice mismatch of $\sim 0.466\%$ (LSAT ($a = 3.868 \text{ \AA}$) and SrFeO₃ ($a = 3.85 \text{ \AA}$)). The full XRD scan shows that SFO films on LSAT are epitaxially grown along (00 l) direction without detectable impurity phase (not shown here). It was observed that the SFO samples have very high resistivity values if measured more than a few days after synthesis. As shown in Figure 1a, the SFO (002) peak shifts towards the smaller 2 θ angle with time, indicating the out-of-plane lattice parameter of SFO thin film grown on LSAT (001) substrate increases

during aging. In order to probe the in-plane lattice variation over time, RSM around LSAT (103) peak was conducted. As shown in Figure 1c and 1d, RSM scans reveal that the in-plane lattice parameter does not show a clear shift when exposed to air at room temperature over a period of 5 days. These results indicate that while the volume of the SFO thin film increases over time, this structural change does not appear to be driven by strain relaxation of the film. The change of the crystal structure often correlates with oxygen content and cation stoichiometry.^{13,17,18} For example, the oxygen vacancies have been directly correlated with the out-of-plane lattice parameter of complex metal oxide thin films.^{19,20} Yamada et al.¹³ argued that the larger out-of-plane lattice parameter of SFO films on STO, compared to films on LAST, is due to the formation of $\text{SrFeO}_{2.5}$ phase on STO and high oxygen content phase on LAST. Oxygen vacancies produce electrons which enter the neighboring d -orbitals of iron reducing the ion from Fe^{4+} to Fe^{3+} and increasing the ionic radius of the Fe ion. Hence, the increase of lattice parameter of SFO films is directly related with the increase of oxygen vacancies. An illustration of the structural dependence of bulk SFO on the oxygen content is presented in Figure 1b. The out-of-plane lattice parameter of SFO on LSAT is 3.83 Å and increases to 3.844 Å with time, which is a change of approximately 0.784 %. RSM data suggests that the in-plane SFO film lattice parameter is approximately 3.90 Å, and does not shift notably during the investigated time period. The XRD and RSM data indicate that the SFO unit cell volume is increasing over 5 days after growth, suggesting that the number of oxygen vacancies in the film is increasing. Hence, the structural change of SFO films with time is directly correlated with the oxygen vacancies.

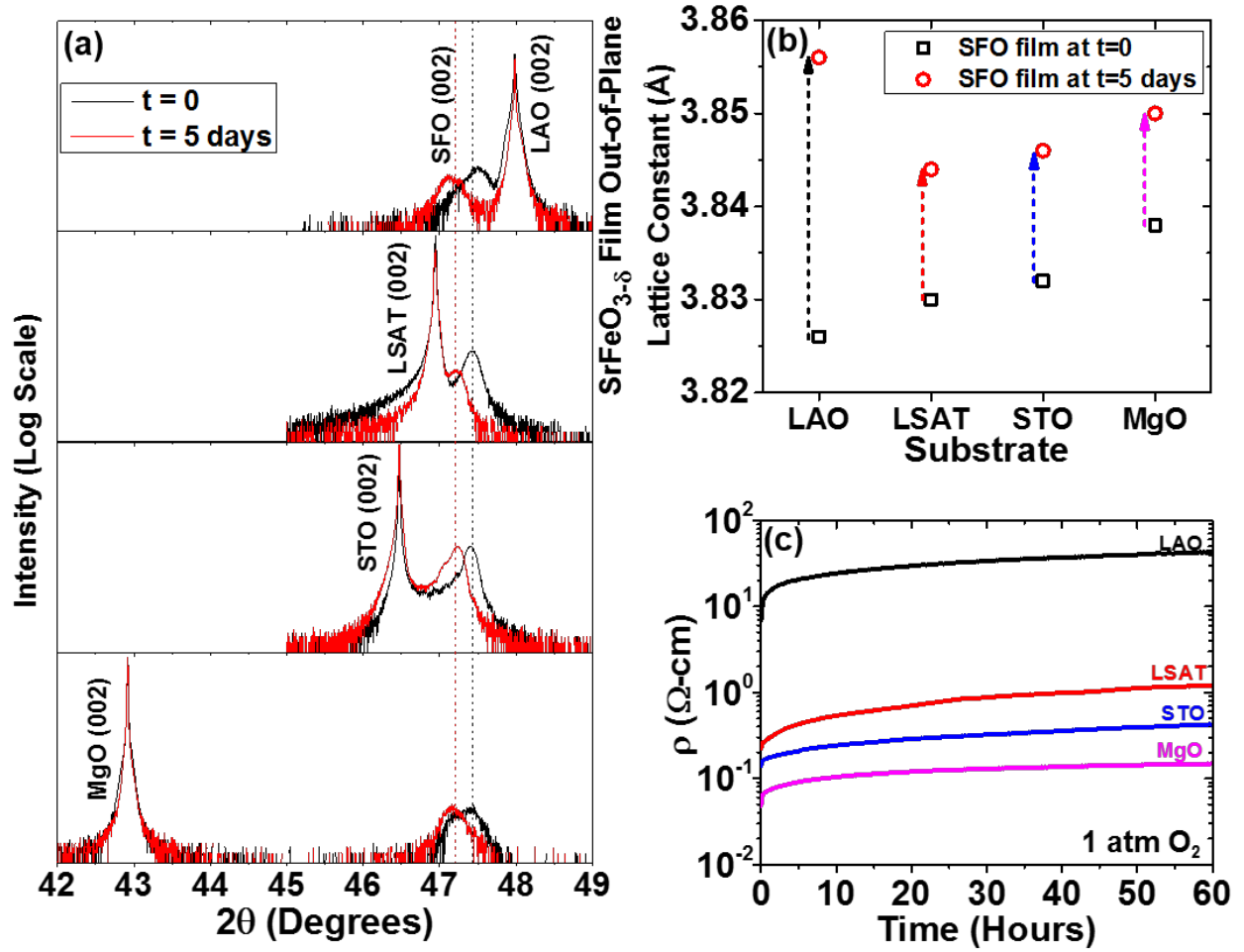


Figure 2. a) 2θ - ω XRD scans of SFO film on LAO, LSAT, STO and MgO substrates at $t = 0$ (black curves) and 5 days (red curves). The dotted lines are used to guide the eye. b) SFO out-of-plane lattice constant (\AA) vs. substrate at $t = 0$ (black squares) and $t = 5$ days (red circles). c) Resistivity vs. time in O_2 for SFO films grown on LAO, LSAT, STO, and MgO substrates.

Table 1. Structural and electrical properties of SFO films grown on LAO, LSAT, STO and MgO substrates, and lattice parameters after 5 days of storage in air.

Substrate	ρ ($\Omega\text{-cm}$) $t = 0$	SFO c -parameter (\AA) $t = 0$	SFO c -parameter (\AA) $t = 5$ days in air
LAO	6.83	3.826	3.856
LSAT	0.223	3.83	3.844
STO	0.139	3.832	3.846
MgO	0.048	3.838	3.85

In addition to LSAT substrate, SFO films were also deposited on LAO, STO and MgO substrates to study the strain dependence of the variation of oxygen content over time. $2\theta-\omega$ XRD scans were utilized to observe changes in the SFO film under various strain conditions on different substrates. As shown in Figure 2a and 2b, the SFO (002) peaks shift to smaller angles indicating that the out-of-plane lattice parameter of SFO increases over time, regardless of the strain state of the film. Interestingly, the initial resistivity of SFO films are extremely sensitive to the out of plane lattice, as shown in Table 1 and Figures 2b and 2c. Films on LAO exhibit the smallest out of plane lattice parameter (3.826 Å) and the largest initial resistivity (6.83 Ω cm). When the out of plane lattice parameter of SFO films on LAST and STO increases to 3.83 Å, the initial resistivity drops over 10 times. The SFO films on MgO exhibit the largest out of plane lattice parameter (3.838 Å) and the smallest initial resistivity (48 mΩ cm), compared to films on other substrates. LAO, LSAT and STO substrates exert an epitaxial strain on SFO films due to the small lattice mismatches. The lattice matched substrates tend to confine the growth. However, MgO does not promote a direct lattice matching due to a large mismatch (~7 %) between SFO and MgO. The large lattice mismatch favors domain matching epitaxy on the MgO substrate. In an oxygen rich growth environment, the growth of SrFeO₃ is more favored rather than SrFeO_{2.5} phase. Therefore, the out-of-plane lattice parameter of SFO films on MgO (3.838 Å) is closer to the SrFeO₃ bulk (3.85 Å) than films on the other three substrates (see Table 1).

The change of resistivity over time has been studied in a dry O₂ flow environment. The SFO films on different substrates are compared, as shown in Figure 2c. In air the SFO samples were observed to change much more rapidly, which may be due to humidity effect, so a dry O₂ flow environment was used to compare the evolution of conductivity over time with the films grown on the selected substrates. Although oxygen vacancies in perovskite oxides can produce charge carriers that contribute to increased conductivity in systems such as SrTiO₃,²¹ several material systems with multiple B-site valence states such as SFO and SrCoO_{3-δ} have oxygen vacancies compensated by changes in B-site valence state and conductivity is not increased in the presence of oxygen vacancies.^{13,22} On all substrates, it is observed that

after an initial rapid rise in resistivity of SFO films the resistivity value begins to saturate with time. For example, SFO on LSAT substrate has an initial resistivity value of $\sim 0.223 \text{ } \Omega\text{-cm}$ and increases to $1.2 \text{ } \Omega\text{-cm}$ over the course of 60 hours in a flow of 1 atm ultra-high purity O_2 . Similar increases are seen in SFO films grown on MgO, STO, and LAO substrates, though it is interesting to note that the substrates mainly affect the initially obtained resistivity values, but not the trend of resistivity change with time. Hence, the variation of resistivity over time is determined by the oxygen vacancy-induced structural change, and the strain state of the thin film does not seem to be a primary driver of further oxygen vacancy generation.

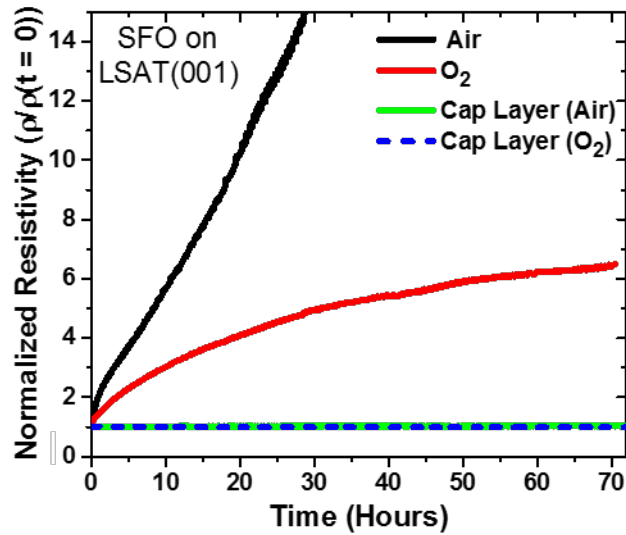


Figure 3. Normalized resistivity vs. time for SFO film grown on LSAT (001) in air and O_2 , in comparison with that of the films covered by a 300 nm Al_2O_3 passivation layer used to keep oxygen in the film.

Resistivity vs. time measurements were carried out in SFO thin film on LSAT in various atmospheres. Figure 3 shows room temperature resistivity over time in O_2 and air environments for SFO/LSAT. The resistance change over time follows an almost logarithmic trend in O_2 , while in air the trend follows a loosely linear behavior with a much greater rate of change in the investigated range. Over the course of 72 hours, the resistivity of SFO grown on LSAT is shown to increase to approximately 650%

of the original value in O_2 , but in air the value increased to 650% in about 12 hours. The greater rate of resistivity change could be due to the interaction of the film with humidity in the air, which was measured to be an average of ~20% during the period of measurement. Although the resistivity tends to saturation in the dry O_2 flow, in air the resistivity continues to rise rapidly beyond our measurable range with no clear sign of saturation. Therefore, the ambient environment of the SFO thin film is the key to influence the resistivity change over time.

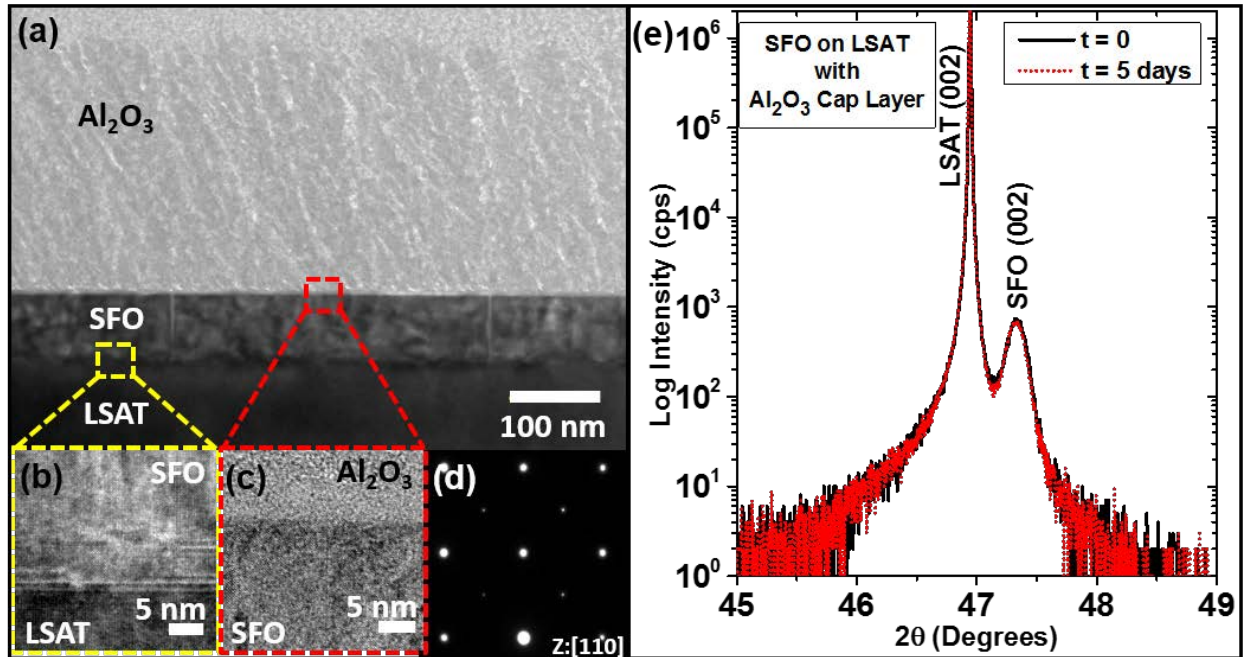


Figure 4. Structural characterization of Al_2O_3 passivation layer introduced over SFO film grown on LSAT substrate. a) Cross-sectional TEM image of Al_2O_3 /SFO/LSAT structure, b) TEM zoom of SFO/LSAT interface, c) TEM zoom of Al_2O_3 /SFO interface and d) SFO/LSAT interface along [110] Zone axis. e) 2θ - ω XRD scan at $t = 0$ (black curve) and $t = 5$ days (red dotted curve).

An Al_2O_3 passivation layer was introduced in attempt to stabilize SFO thin films. The SFO thin film with passivation layer was characterized by cross-section TEM and SAED, as shown in Figure 4a-4d. The TEM results show that the SFO film is approximately 75 nm in thickness, with good delineation

between layers. The Al_2O_3 passivation layer, with a thickness of approximately 300 nm, is amorphous. Strikingly, the introduction of the amorphous passivation layer stabilizes the resistivity of the SFO thin film, as can be seen from the X-ray diffraction patterns in the green and dashed blue lines in Figure 3. With the addition of the passivation layer, there is no increasing trend in resistivity observed in the SFO thin film in O_2 and air environments at room temperature over the course of 72 hours. This stability is consistent with XRD results. The 2θ - ω scans, as shown in Figure 4e, show that the out-of-plane lattice parameter of SFO (002) does not change with time. This result further demonstrates that the structural and electrical property changes over time are primarily driven by the oxygen loss in the SFO thin films. When SFO films are stabilized by the passivation layer, no variation in structural and electrical properties is observed. These results suggest that incorporating an Al_2O_3 passivation layer is an effective method in stabilization of SFO thin films.

To summarize, we have fabricated SFO thin films on various substrates. We demonstrate that the changes in structural and electrical transport property over time in various conditions are correlated with the loss of oxygen in SFO thin films. The initial resistivity of the film relies heavily on the substrate on which it is grown, while strain is not shown to be the main contributing factor in the rate of resistivity increase over time in the SFO thin film. An Al_2O_3 passivation layer has been demonstrated to be an effective approach to stabilize oxygen content, and thus the crystal structure and electrical conductivity of SFO thin films. Our results mark an important step towards stabilization of the SrFeO_3 metallic phase in thin films for research and technological applications.

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